Electronic Supplementary Information (ESI)

High-yield preparation of polystyrene/silica clusters of controlled morphology

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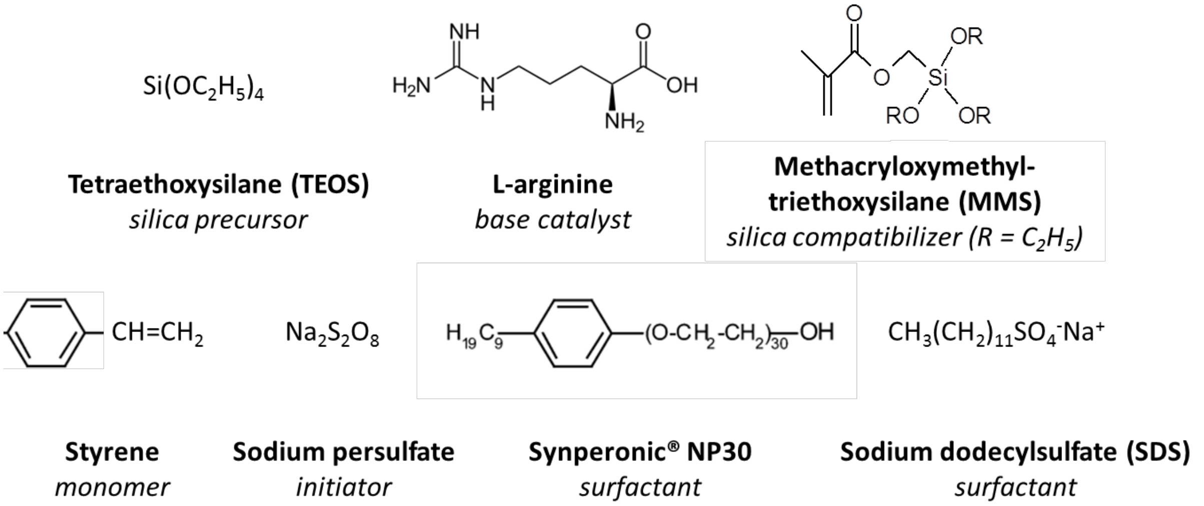
Experimental section

Materials

Tetraethoxysilane (TEOS, 99 %, Aldrich), L-arginine (98.5 %, Aldrich), ammonium hydroxide (28-30 % in water, J. T. Baker), absolute ethanol (99.9 %, Scharlau), styrene (99 % purity, inhibited with 4-tert-butylcatechol, Aldrich), methacryloxymethyltriethoxysilane (97 %, ABCR), Synperonic® NP30 (Aldrich), sodium dodecylsulfate (99 %, Aldrich) and sodium persulfate (99 %, Aldrich) were used without further purification. Ultrapure water (18.2 MOhm.cm at 25°C) was obtained with a Direct-Q3 system (Millipore).



Scheme S1. Chemical structures of the main chemicals used in this study.

Silica seed synthesis and surface modification

Silica "pre-seeds" were obtained according to a previously published recipe where TEOS was slowly hydrolyzed at the surface of a L-arginine aqueous solution [K.D. Hartlen, A.P.T. Athanasopoulos and V.Kitaev, *Langmuir,* 2008, **24**, 1714]. Typically, 100 mL of L-arginine aqueous solution (6 mM) were added in a 150-mL vial thermostated with hot water circulation at 60°C and equipped with a reflux condenser and a 3-cm Teflon®-coated stirring bar. When the constant temperature of 60°C was reached, a chosen volume of TEOS was gently added in order to create a top organic phase. The stirring rate was adjusted in order to maintain the organic phase undisturbed and the aqueous phase efficiently mixed (~150 rpm). The reaction was stopped 2 h after the organic phase had completely disappeared. Silica concentrations were determined by gravimetric analysis from dried extracts. In a given volume, the number of silica seeds N_{silica} was calculated from the silica concentration and the particle average diameter and assuming that the particles were spherical and their density was 2.2. Regrowth stages were performed at room temperature in a conventional glass flask where 250 mL of ethanol, 35 mL of ammonia and 10 mL of the aqueous dispersion of silica "pre-seeds" were successively introduced. The mixture volume was completed to 500 mL with ethanol. Then, a calculated amount of TEOS was added at the rate of 0.5 $mL.h^{-1}$. The mixture was stirred till the completion of the TEOS addition. After checking of the seed size and concentration, the reacting mixture was transferred into a three-neck round flask equipped with a reflux condenser and MMS was added at the concentration of 0.5 $function.nm^{-2}$ of silica (based on the estimate of the silica developed surface area from the average diameter and concentration values). It was let to react for 3 h at room temperature and 1 h at 90°C. The excess ammonia was removed from the reacting medium with the help of a rotary evaporator. Then, particles were purified by dialysis against water until neutral pH in order to remove the remaining reactants and replace ethanol with water. The final concentration of silica seeds was determined by measuring the mass of a dried extract.

Styrene emulsion polymerization

Emulsion polymerization of styrene (100 $g.L^{-1}$) was performed according to unvaried conditions in a thermoregulated reactor under a nitrogen atmosphere, using Synperonic® NP30 (95 wt. %) and sodium dodecylsulfate (5 wt. %) at a total concentration of 3 $g.L^{-1}$ and sodium persulfate (0.5 % w/w relative to monomer). Under a constant stirring at 170 rpm, the reactor was successively filled with water, surfactants, styrene and lastly initiator when the temperature of 70°C was reached. For studying the evolution of the monomer-to-polymer conversion as a function of time by the method of the dried extracts, samples were collected from the batch at different times, the polymerization reaction being quenched by cooling to room temperature.

Preparation of silica/polystyrene clusters by seeded-growth emulsion polymerization

Experiments were performed in the same conditions than those described in the previous section except for the introduction of the aqueous dispersion of silica seeds just before that of the surfactant mixture. Temperature control and stirring were maintained till complete monomer-to-polymer conversion (about 5 h).

Electron microscopy experiments and statistical calculations

TEM images were obtained with a FEI CM120 microscope operating at an accelerating voltage of 120 kV. SEM images were recorded with a JEOL 6700F microscope with an accelerating voltage of 5 kV. Typically, samples were diluted 100 times in ethanol and one drop was deposited on a copper grid coated with a carbon membrane (prior to SEM imaging, the carbon membrane was made electron conductive by sputter-coating with gold/palladium alloy). The average diameter of the silica or PS latex particles was measured directly from the transmission electron micrographs by using the ImageJ software. A minimum of 1000 and 200 objects were counted for each silica and PS latex batch, respectively. The polydispersity index PDI was calculated using the following equation:

$$PDI=\frac{\overline{D_w}}{\overline{D_n}} \quad \text{where } \overline{D_n}=\frac{\sum_i n_i D_i}{\sum_i n_i} \quad \text{and} \quad \overline{D_w}=\frac{\sum_i n_i D_i^4}{\sum_i n_i D_i^3}$$

are the number-average and the weight-average diameter, respectively, and n_i the number of particles of diameter D_i. Statistical analyses of the clusters morphology were performed on a minimum of 600 clusters per batch.

Supplementary figures and tables
(in the order in which they are called from the main text)

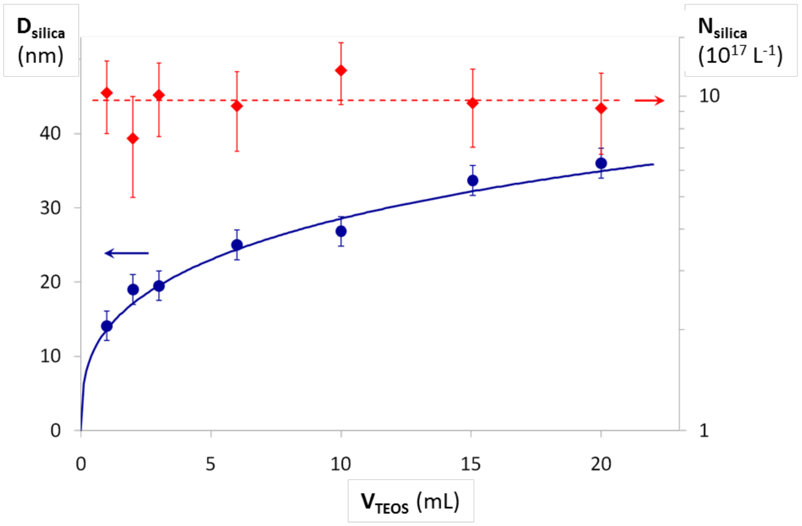


Figure S1. Evolution of the diameter (D_{silica}) and particle concentration (N_{silica}) of silica « pre-seeds » as a function of the added amount of TEOS (V_{water} = 100 mL; $[arginine]_0$ = 6 mM, T = 60°C, stirring speed ~150 rpm]. Average diameter values were extracted from the statistical analysis of TEM images. Error bars were estimated from results of experiments which were repeated three times for V_{TEOS} = 10 mL. An average value of $N_{silica} = (10 \pm 2)*10^{17}$ L^{-1} was determined from all the experiments (dotted line). The solid curve was fitted from the following equation:

$$D_{silica} = \sqrt[3]{\frac{6.V_{TEOS}.d_{TEOS}.M_{silica}}{\pi.N_{silica}.d_{silica}.M_{TEOS}}}$$

considering the density values of d_{TEOS} = 0.93 and d_{silica} = 2.20, and the molar mass values of M_{TEOS} = 208 g.mol^{-1} and M_{silica} = 60.1 g.mol^{-1} and leading to an average number of silica particles of $N_{silica} = 9.1*10^{17}$ L^{-1}. This value is comparable to the average experimental value ($10.2*10^{17}$ L^{-1}). The fact it is slightly lower could be explained by some water evaporation during the experiments.

Table S1. Experimental conditions for the silica regrowth stages and size measurement results of the 85-nm and 55-nm silica seeds (in bold). Average diameter values were extracted from the statistical analysis of TEM images.

Silica "pre-seeds"		1st regrowth stage			2nd regrowth stage (optional)		
D^i_{silica} (nm)	PDI	TEOS/silica (wt. ratio)	measured D^f_{silica} (nm)	measured PDI	TEOS/silica (wt. ratio)	measured D^f_{silica} (nm)	measured PDI
17.3	1.04	80	**53.4**	1.003			
17.3	1.04	80	**53.9**	1.003			
17.3	1.04	80	**54.6**	1.004			
19.0	1.04	81	65.5	1.004	5.4	**85.9**	1.002
19.5	1.02	284	80.2	1.002	0.7	**84.2**	1.002
19.5	1.02	284	81.6	1.002	0.7	**84.8**	1.002
27.5	1.02	82	79.3	1.002	0.8	**86.7**	1.002
27.5	1.02	99	**84.4**	1.002			
28.6	1.02	28	**55.3**	1.003			
28.6	1.02	87	**85**	1.002			
33.7	1.01	52	**87.5**	1.001			

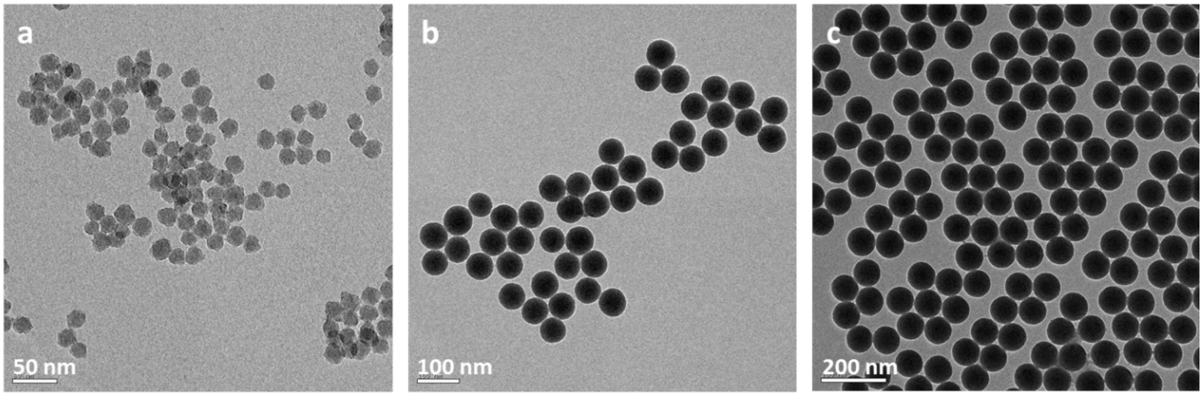


Figure S2. TEM images of (from left to right): a) silica « pre-seeds » (D_{silica} = 19.0 nm; PDI = 1.04), b) silica seeds obtained after a 1st regrowth stage (D_{silica} = 65.5 nm; PDI = 1.004) and c) silica seeds obtained after a 2nd regrowth stage (D_{silica} = 85.9 nm; PDI = 1.002).

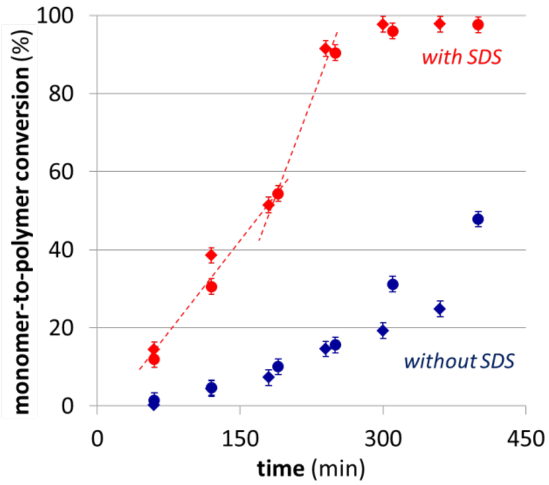


Figure S3. Influence of the substitution for 5 wt.% of Synperonic® NP30 by SDS on the evolution of the monomer-to-polymer conversion as a function of time during the emulsion polymerization of styrene ($[styrene]_0$ = 100 $g.L^{-1}$; $[Na_2S_2O_8]_0$ = 0.5 $g.L^{-1}$; [surfactant] = 3 $g.L^{-1}$; T = 70°C). Each series of data results from the contribution of two identical experiments.

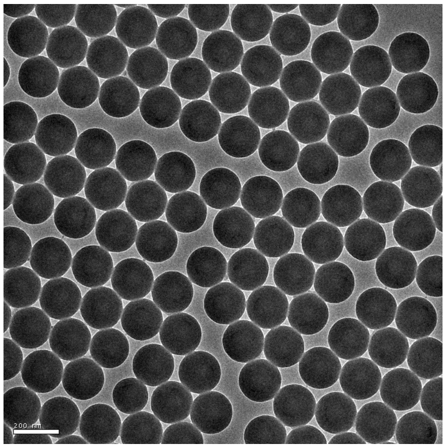


Figure S4. TEM images of PS particles obtained at complete monomer-to-polymer conversion in the case of the substitution for 5 wt. % of Synperonic® NP30 by SDS ($[\text{styrene}]_0$ = 100 g L^{-1}; $[Na_2S_2O_8]_0$ = 0.5 g L^{-1}; [surfactant] = 3 g L^{-1}; T = 70°C). Statistical treatment led to D_{PS} = 184 nm and PDI < 1.001 (scale bar: 200 nm).

Table S2. Experimental conditions for the synthesis of silica/PS clusters from ~85-nm silica seeds and their main morphology features as extracted from the statistical analysis of TEM images.

Batch number *	**Silica seeds**	**Features of the resulting dispersions**				**Proportions of the different clusters made of n PS nodules (% with respect to silica seeds)**				
	D_{silica} (nm)	**N_{PS} (10^{16} L^{-1})**	**D_{PS} (nm)**	**N_{PS}/N_{silica}**	**average $N_{PS/silica}$**	**n ≤ 4**	**n = 5**	**n = 6**	**n ≥ 7**	**with more than one silica core**
# H1	84.2	4.6	152	6.3	5.7	8.0	13.0	75.0	0.0	4.0
# H2	84.4	4.4	155	6.0	5.8	5.0	9.0	79.0	0.0	7.0
# H3	84.8	5.4	141	7.4	5.8	5.0	9.0	85.0	0.0	1.0
# H4	84.8	3.8	156	5.2	5.9	2.0	5.0	91.0	0.0	2.0
# H5	84.8	4.5	151	6.2	5.8	3.0	13.0	83.0	0.0	1.0
# H6	85.9	4.9	145	6.7	5.7	5.0	14.0	78.0	0.0	3.0
# H7	86.7	3.7	160	5.1	5.8	4.0	9.0	78.5	0.0	8.5
# H8	87.5	4.6	150	6.3	5.9	3.0	6.0	84.0	0.0	7.0
# H9	85.0	5.2	144	7.1	5.7	10.0	7.0	82.0	0.0	1.0

* Experimental polymerization conditions: N_{silica} = $7.3*10^{15}$ L^{-1}; $[\text{styrene}]_0$ = 100 $g.L^{-1}$; $[Na_2S_2O_8]_0$ = 0.5 $g.L^{-1}$; [surfactant] = 3 $g.L^{-1}$; T = 70°C; time = 5 h; monomer-to-polymer conversion > 90 %.

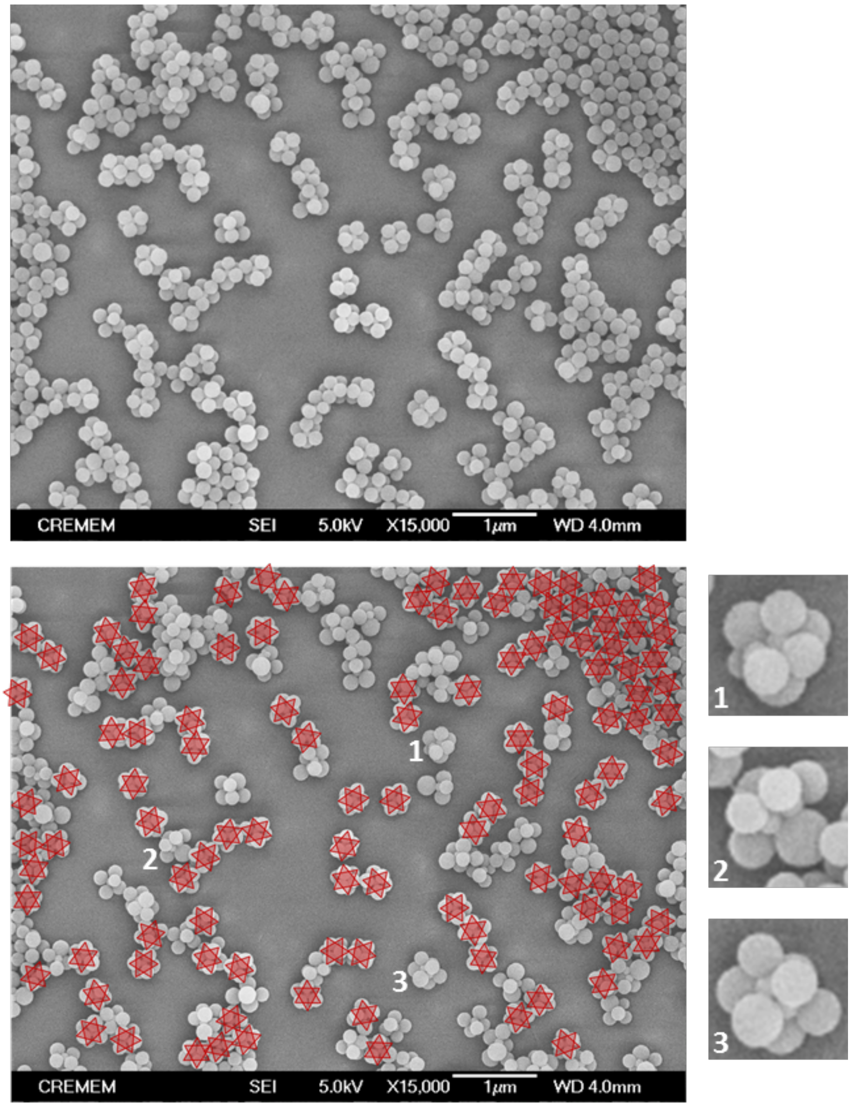


Figure S5. SEM image of hexapods obtained by styrene emulsion polymerization from ~85-nm silica seeds (batch # H8). On the bottom image, the hexapods, which were undoubtedly identified, have been labelled (those whose the image is truncated were not considered) for appreciating the synthesis yield and distinguishing more easily the morphology of by-products: (i) clusters whose pods number is lower than six and which might derive from broken hexapods or hexapods whose several PS nodules have merged (in that situation one of the PS pods is much larger) and (ii) clusters made of more than one silica seed bearing generally a number of pods higher than six (three examples in enlarged images). From this single image, the yield in hexapod morphology was estimated to 61 ± 1 % with respect to silica seeds (116 undoubted hexapods against 54 ± 3 other or unidentified clusters containing 74 ± 4 silica seeds).

Table S3. Experimental conditions for the synthesis of silica/PS clusters from ~55-nm silica seeds and their main morphology features as extracted from the statistical analysis of TEM images.

Batch number*	**Silica seeds**	**Features of the resulting dispersions**				**Proportions of the different clusters made of n PS nodules (% with respect to silica seeds)**				
	D_{silica} (nm)	**N_{PS} (10^{16} L^{-1})**	**D_{PS} (nm)**	**N_{PS}/N_{silica}**	**average $N_{PS/silica}$**	**$n \leq 2$**	**$n = 3$**	**$n = 4$**	**$n \geq 5$**	**with more than one silica core**
# T1	53.4	5.7	141	3.2	3.8	2.0	13.0	80.5	0.0	4.5
# T2	54.6	5.0	144	2.8	3.8	4.0	14.5	76.0	0.5	5.0
# T3	54.6	6.1	146	3.4	3.9	1.5	12.0	82.5	0.0	4.0
# T4	55.3	4.8	146	2.6	3.8	2.0	11.0	84.0	0.0	3.0
# T5	55.3	3.9	152	2.2	3.9	2.0	11.0	81.0	3.0	3.0
# T6	53.9	5.3	141	2.8	3.9	1.5	9.0	80.0	0.5	9.0

* Experimental polymerization conditions: $N_{silica} = 1.8*10^{16}$ L^{-1}; $[styrene]_0 = 100$ $g.L^{-1}$; $[Na_2S_2O_8]_0 = 0.5$ $g.L^{-1}$; [surfactant] = 3 $g.L^{-1}$; T = 70°C; time = 5 h; monomer-to-polymer conversion > 90 %.